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During the past ten years research on lithium batteries has been increasingly directed towards a rechargeable battery system as many primary lithium batteries are now commercially available. Most of the research on the secondary lithium batteries has been on systems with solid insertion cathodes and nonaqueous, liquid organic electrolytes with a wide variety of solvents and compounds having been evaluated. Recent studies on polymer electrolyte systems have resulted in solid state rechargeable lithium cells, operable at 25°C. Capacity decline with cycling and the high internal resistance at low temperatures limit the application of these systems. Continuous work in this area will improve the performance characteristics of these cell systems.

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RECHARGEABLE LITHIUM POLYMER ELECTROLYTE BATTERIES

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During the past ten years research on lithium batteries has been increasingly directed towards a rechargeable battery system as many primary lithium batteries are now commercially available. Most of the research on the secondary lithium batteries has been on systems with solid insertion cathodes and nonaqueous, liquid organic electrolytes with a wide variety of solvents and compounds having been evaluated. Some work also has been reported for inorganic liquid electrolytes in which sulfur dioxide serves as the solvent, and in some cases, also functions as the electroactive cathode element. More recently, the investigations of cells that utilize solid, polymeric electrolyte materials in rechargeable lithium batteries have been reported. For recent reviews of this subject, see Refs. 1 and 2. Much of this work has been directed towards electrolytes based on amorphous complexes of polyethylene oxide with a variety of lithium salts. The same cathodes that have been studied with liquid electrolytes have also been investigated with polymer electrolyte cell systems, especially cathodes of TiS_2 or V_6O_{13}.

Progress on liquid electrolyte rechargeable lithium battery systems has been very good and a number of small coin cells are commercially available. Somewhat larger "AA" size cells also can be procured and the cycle life that one can obtain appears to be in the range of several hundred to over 1,000. Cycle life is very sensitive to a number of factors including rate and depth of discharge. Generally, the cells are designed with excess lithium so that the typical discharge depth on the anode is much less than 100%. Problems with dendritic lithium appear minimal in certain designs and one of the conclusions resulting from work thus far reported is that cycleability of a lithium electrode is favored by use of thin electrodes with low loadings of lithium that may consequently be cycled at fairly low current densities, even under high rate conditions. This property favors the design of polymer electrolyte cells which are required to be ultra-thin to mitigate the relatively high resistance of the solid electrolyte.

Many advantages have been cited in the past for all solid state batteries. Nonetheless, practical batteries of this design are few in number. The lithium/lithium iodide/iodine pacemaker battery has been described as a "solid state" battery. However, it was shown that the performance of such batteries was facilitated by the presence of a liquid interfacial electrolyte film that forms in-situ between the lithium and the cathode. The role of the interfaces in an all solid state battery is crucial in maintaining internal continuity and charge transport. A second problem with solid state batteries is that as the volume changes in the electrodes during discharge, separation at the interfaces and cracking of the cell can result. The polymer electrolyte has proven to be outstanding in its ability to resolve the previously mentioned problems. The adhesive, elastomeric nature of the polymer complex provides good contact with both the anode and cathode. As these volume changes occur within the battery, there is enough plasticity in the polymeric electrolyte to accommodate the changes while maintaining good electrical contact within the cell.

Further, the requirement for a thin cell results in a low current density such as 1 mA/cm^2 being equivalent to discharge at the C rate. Solid state polymer electrolyte batteries have been shown to cycle hundreds of times in deep discharge without dendritic problems.

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Post mortem examination of cells after 100 cycles has shown that the morphology of the lithium and the cathode at their respective interfaces with the electrolyte have been very homogeneous and smooth. Selection of appropriate salts to complex with the polyether matrix yields electrolytes with large decomposition potentials that permit high voltage cell designs in combination with good cycle life.

Disadvantages with polymer electrolyte batteries have included the requirement that they must operate at elevated temperatures, above the eutectic in the polymer-salt system. Therefore, most of the investigations have been in the temperature interval from 80° - 120°C. The high level of interest in the ambient temperature battery has resulted in the study of many possibly lower temperature electrolyte systems. Recently, the reports of systems that can operate at 25°C were summarized (1). Continuing improvements in this area are expected and it is possible that commercially successful ambient temperature systems will results.

Another problem that has been frequently described is the cell capacity decay associated with continued cycling. The capacity per cycle is reduced and with some designs it was difficult to obtain 100 cycles before the capacity was reduced to 50% of its initial capacity. Again, considerable improvement in this performance characteristic has been achieved and several hundred cycles are claimed under some conditions. More work in this area is being performed.

Because of the availability of many insertion compounds for lithium and the wide stability window for many of the polymeric electrolytes, many cathodes can be considered for batteries. The authors' programs at their respective universities have dealt primarily with LiV_3O_8 at the University of Rome and V_6O_{13} at the University of Minnesota. Some properties of these two electrode couples are compared in Table I.

Table I. Lithium-Cathode Couple Properties

Material	Discharge Product	Theoretical Energy Density (Wh/kg)	Theoretical Energy Density (Wh/dm^2)
V_6O_{13}	$Li_8V_6O_{13}$	800	1900
LiV_3O_8	$Li_4V_3O_8$	730	2500

Small polymer electrolyte cells were fabricated with a total cell thickness of 100 microns. Investigations of these cathodes in lithium cells are in progress to identify the unique role of the electroactive elements. It has been found that morphological properties of components, the cell formation processes and impurities can overwhelm the chemical differences of the electroactive materials. The studies are continuing to provide information about long-term behavior and the ultimate usefulness of lithium polymer electrolyte rechargeable batteries.

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